



**AFRL-RX-WP-TM-2008-4218**

**TECHNICAL OPERATIONS SUPPORT (TOPS) III  
Delivery Order 0007: Chalcopyrite Crystal Growth**

**Arnold Burger**

**Fisk University**

**DECEMBER 2007  
Final Report**

**Approved for public release; distribution unlimited.**

*See additional restrictions described on inside pages*

**STINFO COPY**

**AIR FORCE RESEARCH LABORATORY  
MATERIALS AND MANUFACTURING DIRECTORATE  
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750  
AIR FORCE MATERIEL COMMAND  
UNITED STATES AIR FORCE**

## NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report was cleared for public release by the Wright-Patterson Air Force Base (WPAFB) Public Affairs Office and is available to the general public, including foreign nationals. Copies may be obtained from the Defense Technical Information Center (DTIC) (<http://www.dtic.mil>).

THIS REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

\*//signature//

---

JONATHAN GOLDSTEIN, AFRL/RXPS  
Work Unit Manager

//signature//

---

CHRISTOPHER J. RISTICH, AFRL/RXPS  
Branch Chief

//signature//

---

KRISTINE L. TITTLE, AFRL/RXP  
Deputy Division Chief

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government's approval or disapproval of its ideas or findings.

\*Disseminated copies will show “//signature//” stamped or typed above the signature blocks.

<b>REPORT DOCUMENTATION PAGE</b>					<i>Form Approved</i> OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. <b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</b>						
<b>1. REPORT DATE (DD-MM-YY)</b> December 2007		<b>2. REPORT TYPE</b> Final		<b>3. DATES COVERED (From - To)</b> 01 November 2005 – 01 August 2006		
<b>4. TITLE AND SUBTITLE</b> TECHNICAL OPERATIONS SUPPORT (TOPS) III Delivery Order 0007: Chalcopyrite Crystal Growth				<b>5a. CONTRACT NUMBER</b> FA8650-05-D-5807-0007		
				<b>5b. GRANT NUMBER</b>		
				<b>5c. PROGRAM ELEMENT NUMBER</b> 62102F		
<b>6. AUTHOR(S)</b>  Arnold Burger				<b>5d. PROJECT NUMBER</b> 4348		
				<b>5e. TASK NUMBER</b> RG		
				<b>5f. WORK UNIT NUMBER</b> M07R5000		
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b>  Fisk University Department of Physics 1000 17 <sup>th</sup> Avenue N Nashville, TN 37208				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>		
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>  Air Force Research Laboratory Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force				<b>10. SPONSORING/MONITORING AGENCY ACRONYM(S)</b> AFRL/RXPSO		
				<b>11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)</b> AFRL-RX-WP-TM-2008-4218		
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> Approved for public release; distribution unlimited.						
<b>13. SUPPLEMENTARY NOTES</b> PAO case number WPAFB 08-0147, cleared 23 January 2008.						
<b>14. ABSTRACT</b> <p>1. Chalcopyrite crystal growth - AgGaSeTe was grown via Accelerated Crucible Rotation Technique (ACRT). ACRT did provide good homogeneity and elimination of bulk bubbles, however overall crystal quality was inferior to crystals grown by Horizontal Bridgman technique. The anisotropic expansion of AgGaSeTe results in better growth in horizontal configurations which leave a degree of freedom for expansion and contraction along the long, unrestricted (top) side of the crystal. AgGaSe<sub>2</sub> and AgGa<sub>0.6</sub>In<sub>0.4</sub>Se<sub>2</sub> was grown using horizontal Bridgman. Characterization via photoluminescence, optical transmission, and Raman indicate high crystal quality.</p> <p>2. LiGaX<sub>2</sub> crystal growth - LiGaTe<sub>2</sub> and LiGaSe<sub>2</sub> were grown using horizontal electrodynamic gradient technique with a 24-zone furnace. Li could not be obtained with purity better than 99.99%. Synthesis and crystal growth were done in the same carbon-coated vessel, in order to accommodate the high reactivity of Li with the ampoule walls and with air.</p> <p style="text-align: right;"><i>-- Continued on back --</i></p>						
<b>15. SUBJECT TERMS</b>						
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT:</b> SAR	<b>18. NUMBER OF PAGES</b> 18	<b>19a. NAME OF RESPONSIBLE PERSON (Monitor)</b> Dr. Jonathan Goldstein	
<b>a. REPORT</b> Unclassified	<b>b. ABSTRACT</b> Unclassified	<b>c. THIS PAGE</b> Unclassified			<b>19b. TELEPHONE NUMBER (Include Area Code)</b> (937) 255-9785	

#### 14. ABSTRACT, concluded

The LiGaTe<sub>2</sub> crystal was of good optical quality for a first attempt at this material, however only a small single crystal could be mined from the polycrystalline ingot that resulted from the growth attempt. A larger crystal was obtained from the LiGaSe<sub>2</sub> growth, but its optical quality was very poor.

3. GaTe crystal growth - GaTe, GaSe<sub>0.2</sub>Te<sub>0.8</sub>, GaSe<sub>0.8</sub>Te<sub>0.2</sub>, and GaSe were grown via vertical seeded Bridgman, resulting in large crystals of good quality. Optical band gaps were measured by optical transmission and photoluminescence. These results are encouraging that further work could result in a ternary crystal with improved terahertz nonlinear optical performance over GaSe.

## **Final Technical Report for the TOPS III efforts on growth of crystals for infrared applications**

**PI:** Arnold Burger

Department of Physics

Department of Physics, Fisk University

1000 17th Avenue N.

Nashville, TN 37208

Ph. 615-329-8516, FAX 615-329-8634, aburger@fisk.edu

### **D) Chalcopyrite Crystal Growth (\$80k)**

1) Setting up an Accelerated Crucible Rotation Technique (ACRT) and AgGaSeTe

For the growth of nonlinear optical material AgGaSeTe (AGST) was investigated for frequency-doubling the output of CO<sub>2</sub> lasers into mid-infrared spectral range.

- The accomplishments in this project were:
  - a) material synthesis procedure. Stoichiometric charge of elements was sealed under vacuum of  $1.5 \times 10^{-7}$  torr. Heated up to 800 °C at a rate of 60/hr, soaked for 18 hrs. Ampule was kept at ~450 and rotated at 20 rpm. Cooldown at a rate of 60/hr
  - b) Efficient mixing can achieved through the use of Accelerated Crucible Rotation Technique (ACRT) shown in Figure 1, whereby the molten charge is rotated back and forth in manner similar to that of a washing machine. The effectiveness of ACRT is strongly affected by the interaction of rotational forces with buoyant forces. Our assumption is that a better homogeneity of the liquid composition can be achieved resulting in a better uniformity of the grown crystals. [ Ref: H. J. Scheel, Accelerated crucible rotation: A novel stirring technique in high temperature solution growth, Journal of Crystal Growth, Volumes 13-14, May 1972, Pages 560-565 ] Crystal growth was attempted however due

to the vertical configuration inherent to this technique the crystals were inferior to the ones grown by us from the same starting materials and using a parallel system at Fisk in horizontal configuration. We explain these results as being caused by the anisotropic behavior of the thermal expansion of the crystals being more confined to the crucible walls in the vertical geometry. Good mixing was obtained by ACRT by changing the direction of rotation and resulting in bulk bubble elimination. However bubbles still existed on the surface of the ingot, next to the fused silica wall. Unfortunately, the vertical geometry of ACRT is also less amenable to seeding.

- We have successfully grown single crystals of  $\text{AgGaSe}_2$  and  $\text{AgGa}_{1-x}\text{In}_x\text{Se}_2$  ( $x = 0.1-0.3$ ) quaternary crystals using horizontal Bridgman technique. The synthesis of  $\text{AgGa}_{0.6}\text{In}_{0.4}\text{Se}_2$  has been completed and the crystal growth is underway. The synthesis and growth of the crystals were carried out at  $850-900^\circ\text{C}$  using elemental Ag, Ga, In, and Se. The stoichiometry of the grown crystals was evaluated using EDAX measurements. The grown AGS and quaternary crystals were fully characterized by Photoluminescence, optical transmission and Raman spectroscopy along the growth direction and cross-sections.



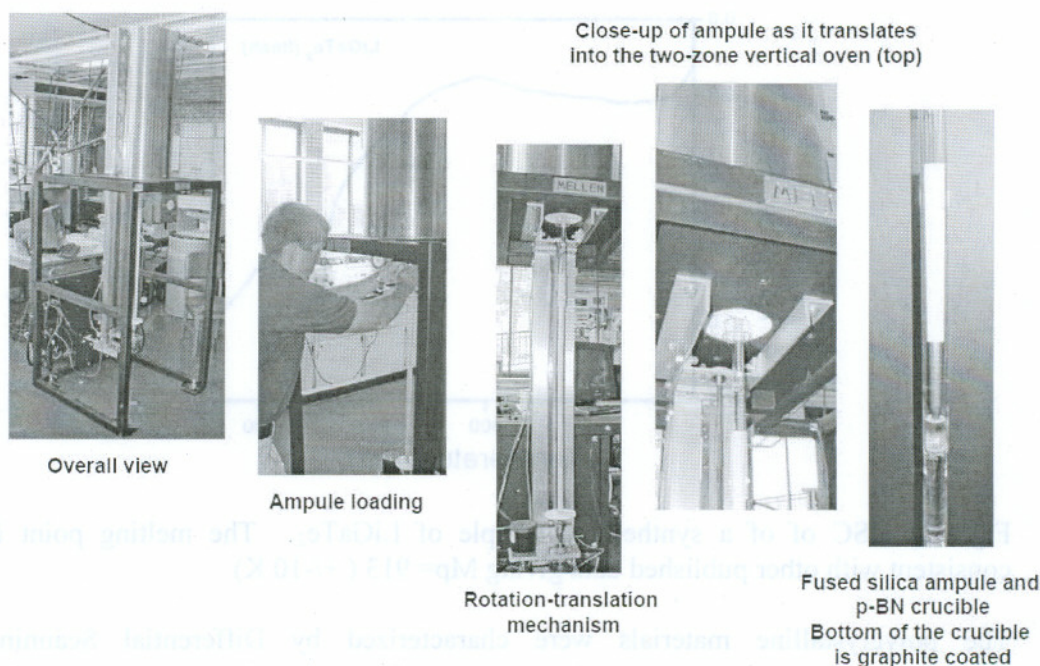


Figure 1. ACRT system at Fisk.

## II) LiGaX<sub>2</sub> Crystal Growth (\$50k)

Recently, growth of the noncentrosymmetric, chalcopyrite structure crystals of Li based nonlinear crystals such as LiGaTe<sub>2</sub> and LiGaSe<sub>2</sub> has attracted much attention due to several remarkable nonlinear properties. Synthesis and growth of LiGaSe<sub>2</sub> and LiGaTe<sub>2</sub> was carried out in glassy carbon crucible around 600-650<sup>0</sup>C by electrodynamic gradient technique (EDG) using 24-Zone furnaces. Polycrystalline with small grain crystal was obtained. The purity of Li is at best of 99.99% and it is regarded as the major impediment in realizing higher quality optical material. Both synthesis and growth are carried out in carbon glassy crucible without breaking the vacuum due to high chemical reactivity of Li containing compound with fused silica tube.

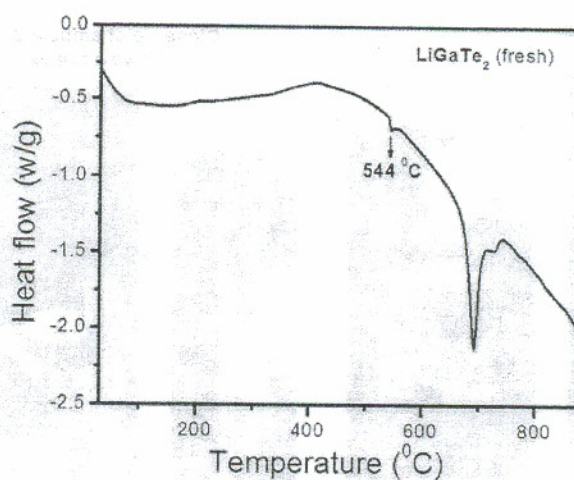


Fig. 2. DSC of of a synthesized sample of  $\text{LiGaTe}_2$ . The melting point is consistent with other published data giving  $M_p = 913$  ( $\pm 10$  K)

The polycrystalline materials were characterized by Differential Scanning calorimetry (DSC) shown in Fig 2. Alumina crucible was used in the temperature range from room temperature to 900  $^{\circ}\text{C}$  at 1 atm. of flowing dry nitrogen.

A  $\text{LiGaSe}_2$  ingot and wafers are shown in Figure 3. The temperature gradient was 10  $^{\circ}\text{C}/\text{cm}$  and the temperature profile moved to obtain a growth rate of 0.5 cm/day.

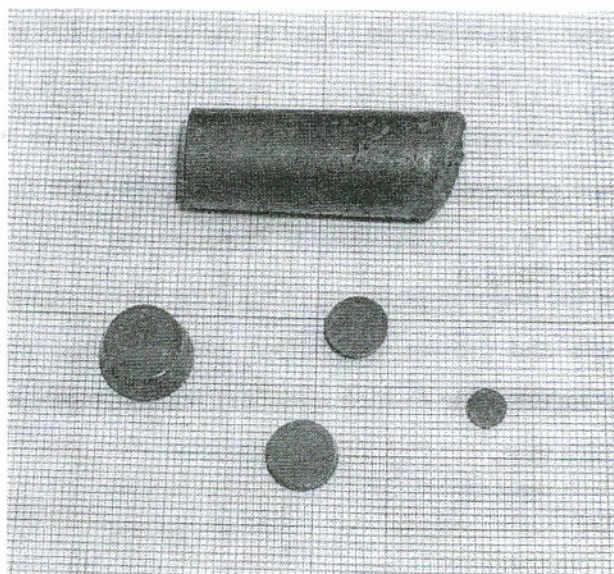


Fig. 3. Ingot and wafers of  $\text{LiGaSe}_2$  grown in this project.



In the  $\text{LiGaTe}_2$  system, we have obtained small grain polycrystalline LGT crystals. Isenko et al. [I. Isaenko, P. Krinitsin, V. Vedenyapin, A. Yelisseyev, A. Merkulov, J. J. Zondy and V. Petrov. *Crystal Growth and Design*, 5,1325 (2005). also. I. Isaenko, I. Vasilyeva, A. Merkulov A. Yelisseyeva, S. Lobanov, *J. of Crystal Growth*, 275, 217 (2005).] reported that they used Ar overpressure to prevent the dissociation of  $\text{LiGaTe}_2$  during Bridgman growth. The high reactivity of Li with ampoules and air along with low purity may prevent for obtaining large single crystal (larger than the one shown in Figure 4) for LGT. We could obtain larger crystals of  $\text{LiGaSe}_2$  however their optical transparency was quite poor.

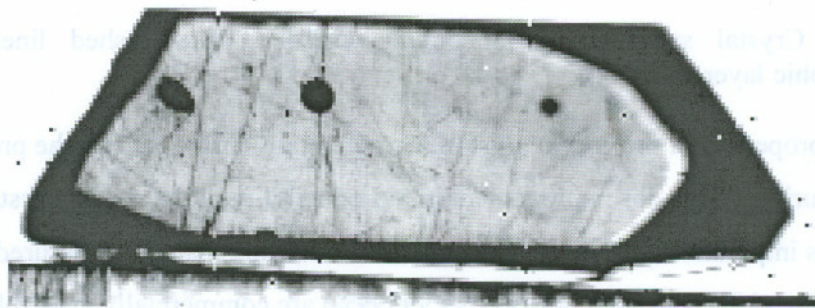


Fig. 4 Near-IR photo of a  $\text{LiGaTe}_2$  crystal (3mm X1.5 mm)

### III) GaTe Crystal Growth (\$35k)

- GaTe has a centrosymmetric monoclinic crystalline structure that is arranged into planes, shown in Fig. 5, where van der Waals bonds occur between the Te terminated planes. There are both Ga-Te and Ga-Ga bonds within the planes of GaTe. Ga vacancies have been suggested to give rise to a shallow acceptor level at 0.15-0.18 eV above the valence band, which causes the material to be exclusively p-type. GaTe is a stable compound, melts congruently and has no solid-state transitions [Yves Feutelais, Bernard Legendre, "Binary phase diagrams of tellurium and post-transitional elements (IB, IIB, IIIB, IVB, VB, VIB)" *Thermochimica Acta* 314 (1998) 35-53]

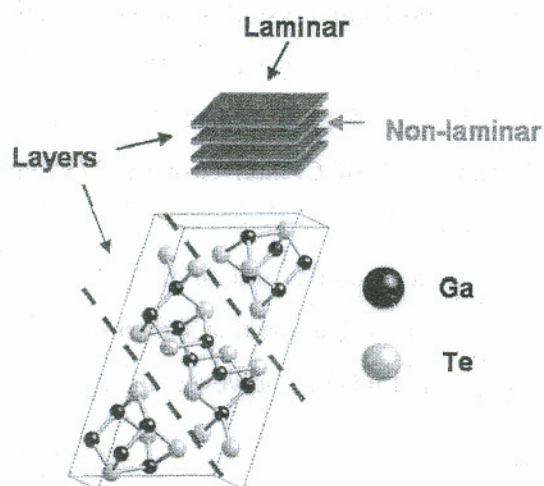


Fig. 5. Crystal structure of monoclinic GaTe. Blue dashed lines indicate crystallographic layers.

The optical properties of the grown crystals are potentially influenced by the presence of residual impurities. Thus for improvement in reproducibility of the grown crystal qualities, it is imperative that the purity ( $>6N$ ) of the starting material is assured.

Elemental Ga and Te with high purity ( $>99.99999\%$ ) are commercially available. GaTe crystals were grown using stoichiometric amounts of high purity (7N) Ga and 7N zone refined Te as starting materials to make a homogeneous polycrystalline ingot.

The synthesis was carried out at  $900\text{ }^{\circ}\text{C}$  (melting point was determined to be  $826\text{ }^{\circ}\text{C}$  using Differential Scanning Calorimetry) for 12 h. The charge was slowly heated at a rate of  $0.4\text{ }^{\circ}\text{C}/\text{min}$  in tubular resistance heated furnace. The charge materials are continuously rotated for uniform mixing, at an angle of  $\sim 45^{\circ}$  with constant rotation of the ampoule  $\sim 20\text{ rpm}$ . After complete synthesis, the ampoule was cooled to room temperature. One of the undoped crystals obtained is shown in Figure 6.

The polycrystalline ingot was then placed in a conically tipped thick-walled ( $\geq 3\text{ mm}$ ) carbon coated quartz ampoule and sealed under a vacuum of  $10^{-6}\text{ torr}$ . The conical tip was specially designed to initiate and hold a GaTe seed crystal, which prevents secondary nucleation and allow growth along a preferred orientation. An axial low temperature gradient ( $\sim 10^{\circ}\text{C}/\text{cm}$  at the growth zone) was imposed by tuning the input power



distribution into the heater to stabilize the solid-liquid interface. The sealed ampoule was then suspended in the Bridgman crystal growth furnace and connected to a slow-speed (0.2 rpm) motor. After which, the polycrystalline material was heated slowly ( $\sim 10^\circ\text{C/hr}$ ) to  $980^\circ\text{C}$  for GaTe in computer controlled three-zone vertical furnace. A computer-operated pre-programmed controller regulates its translational downward motion while the crystal is directionally solidified.

The identical growth procedure was also used for the preliminary growth of the ternary  $\text{GaSe}_{1-x}\text{Te}_x$  crystal with potential nonlinear optical activity. For values of  $x$  between 0.1 and 0.3 it is expected that the system should crystallize in the noncentrosymmetric hexagonal structure of GaSe.

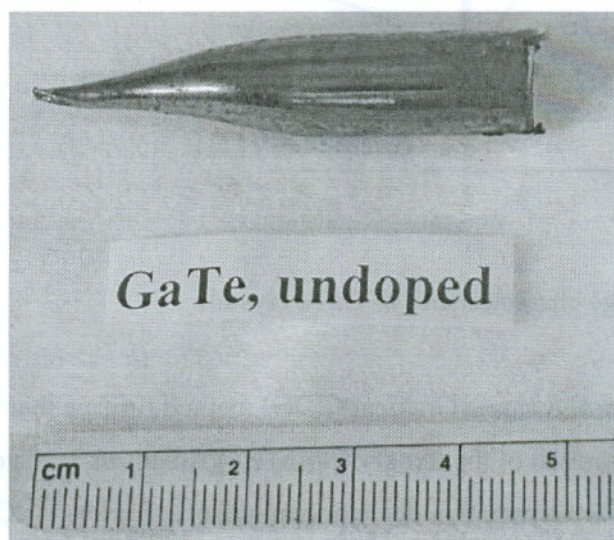


Fig. 6. Photograph of an undoped single crystal of GaTe

The room temperature resistivity of the as-grown and vacuum and Te-annealed GaTe crystals were also measured from current-voltage characteristics as shown in Figure 7

	Resistivity (ohm-cm)
1) GaTe- undoped	$5 \times 10^1$
2) GaTe-Undoped Annealed (7 days)	
a) at 350 C in Vacuum	$8 \times 10^1$
b) Annealed at 350 °C in Te overpressure	$3 \times 10^4$

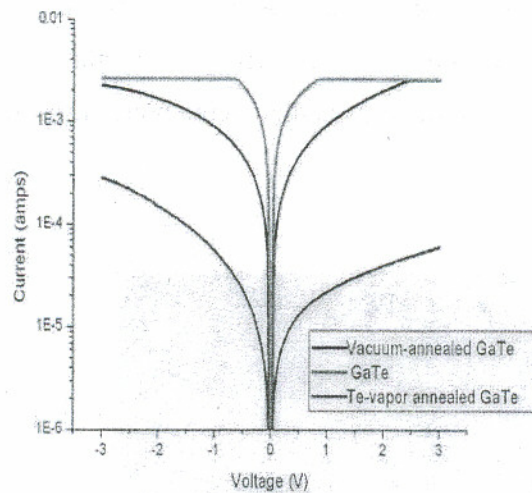


Fig. 7 Current-voltage characteristics of GaTe crystals

GaTe using the ElectroDynamic Gradient (EDG) method furnace that was described in the literature for the growth of the ternary CdZnTe. [Advances in the crystal growth of semiinsulating CdZnTe for radiation detector applications, Szeles, C.; Cameron, S.E.; Nday, J.-O.; Chalmers, W.C. Nuclear Science Symposium Conference Record, 2001 IEEE Volume 4, Issue , 2001 Page(s):2424 – 2428]. The system is PC controlled and allows an operator to enter a desired thermal gradient and its translation rate. The growth occurs without any moving parts. EDG technique nearly completely eliminates the uncontrolled radiative heat transport commonly encountered in traditional Bridgman systems where the charge and furnace move relative to each other. The cooling rate was 1 C/h up to 700 C then 6 C/h to 20 C. The ingots consist of single crystal with the cleavage plane parallel to growth axis. We have also noticed that the last-to-freeze section was slightly concave. The ingots will be cut (diamond impregnated steel wire)

perpendicular to the growth axis then the sections were further cleaved perpendicular to the growth plane.

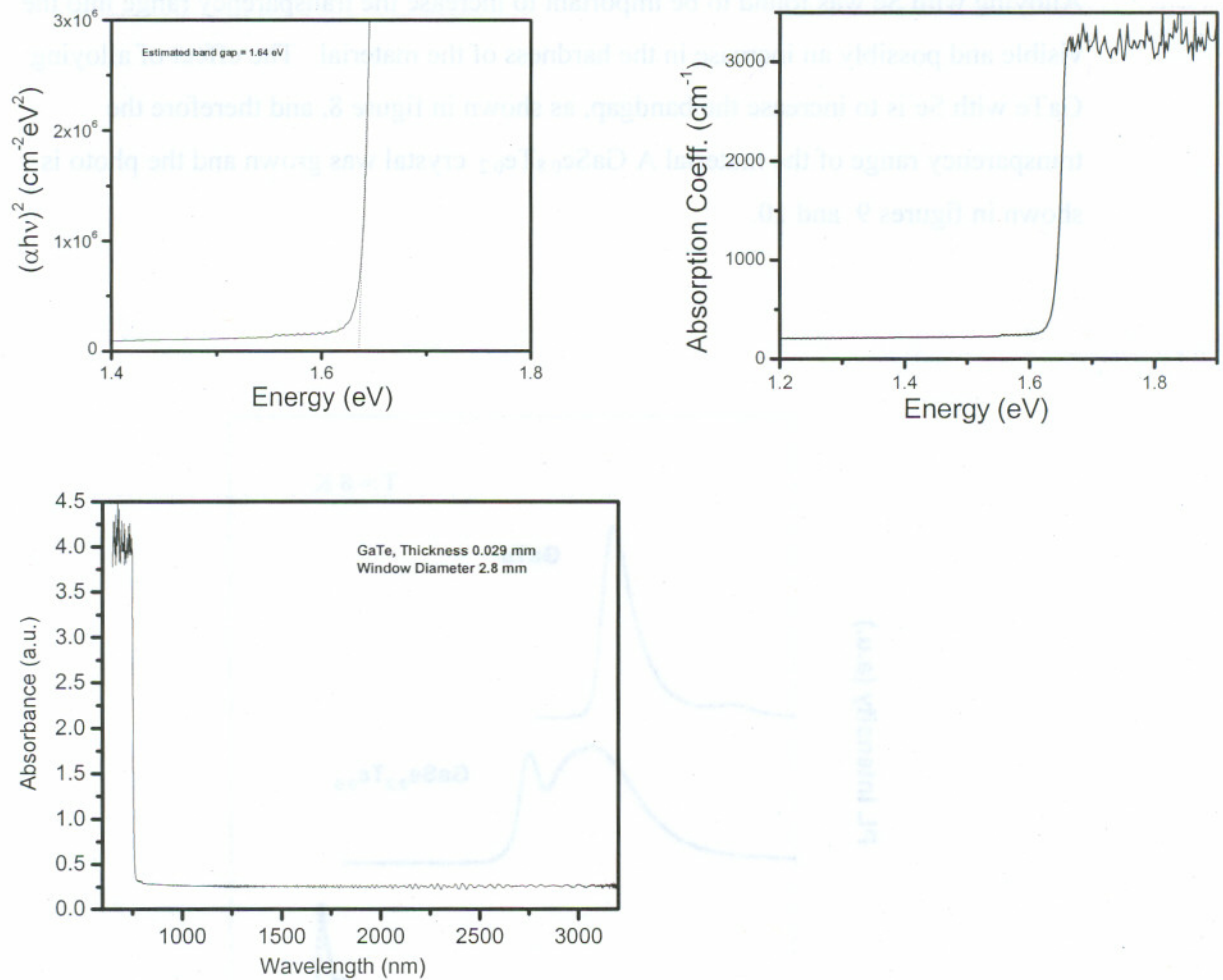


Fig. 7 Absorbance spectrum of GaTe in the near and mid-IR

The thickness was 0.029 mm, measured by SEM. The value of the band gap of GaTe is 1.67 eV and consistent with past literature data. [M. Abdel Rahman and A.E. Belal "Single crystal growth and optical energy gap of gallium telluride," J. Phys. and Chem. of Solids, vol. 61, no. 6, pp. 925-929 (2000)]



Finally, in consultation with Dr. Goldstein at AFRL we have decided that increasing the selenium composition to  $\text{GaSe}_{0.8}\text{Te}_{0.2}$  would be even more beneficial regarding the nonlinear optical properties.

Alloying with Se was found to be important to increase the transparency range into the visible and possibly an increase in the hardness of the material. The effect of alloying GaTe with Se is to increase the bandgap, as shown in figure 8, and therefore the transparency range of the material. A  $\text{GaSe}_{0.8}\text{Te}_{0.2}$  crystal was grown and the photo is shown in figures 9 and 10.

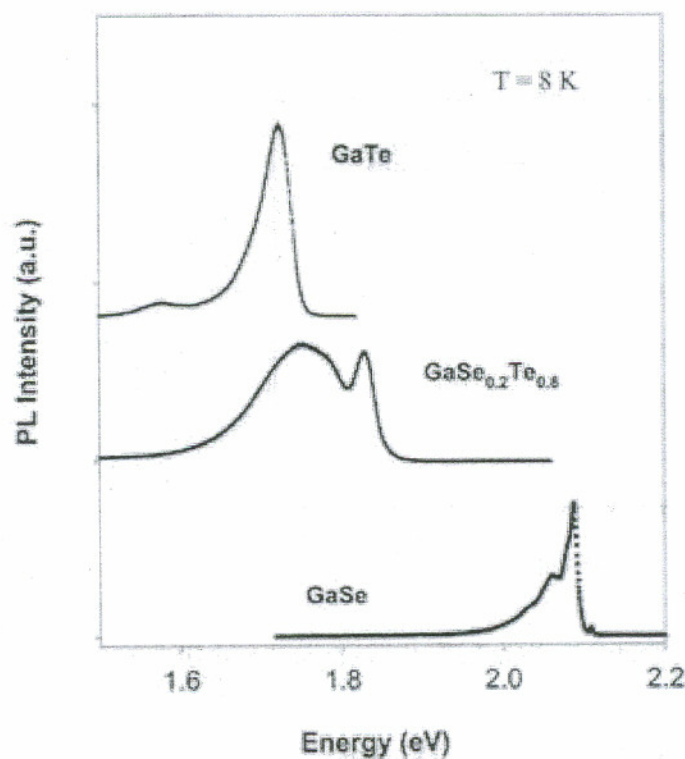


Figure 8. Low temperature photoluminescence of GaTe, GaSe (EIC) and  $\text{GaSe}_{0.8}\text{Te}_{0.2}$ . The effect of alloying GaTe with Se is to increase the bandgap and therefore the transparency range of the material.



Figure 9. Photograph of a  $\text{GaSe}_{0.2}\text{Te}_{0.8}$  crystal after being sectioned with a wire saw.

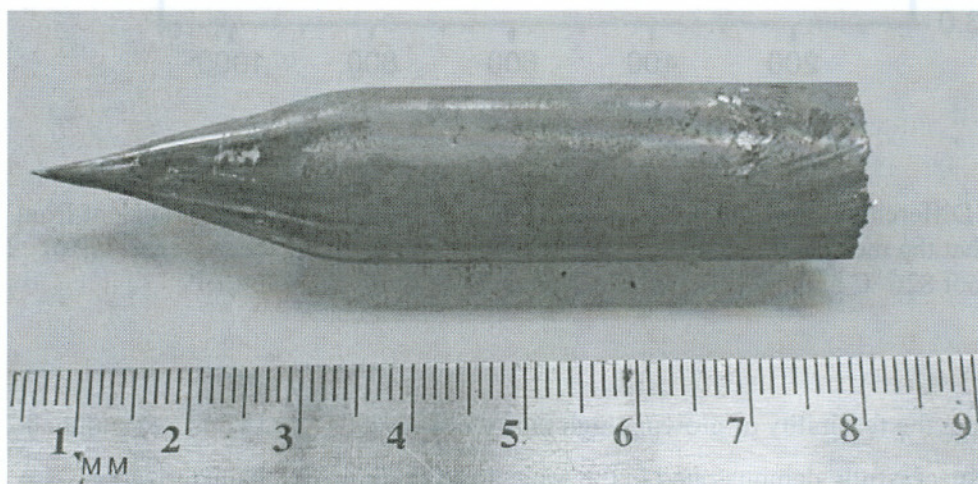


Figure 10. Photograph of an as-grown ingot of  $\text{GaSe}_{0.8}\text{Te}_{0.2}$

A phase change is also observed just below the MP of the material as shown in Figure 11. This phase change restricts the fast growth of the crystal, and eventually, the crystal is being grown at a very slow rate.

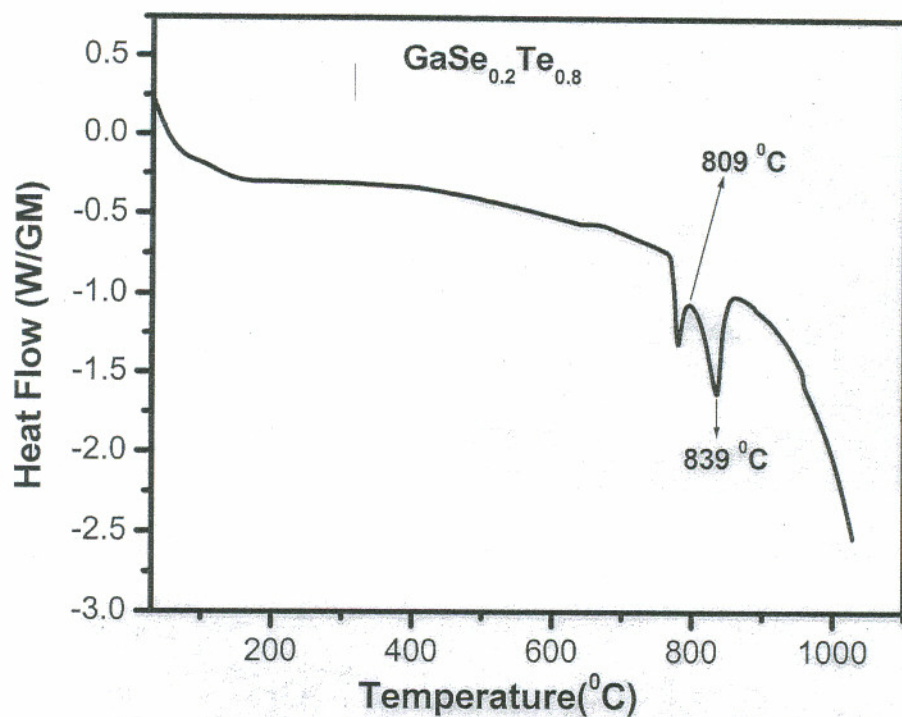


Figure 11. Differential Scanning Calorimetry (DSC) of  $\text{GaSe}_{0.2}\text{Te}_{0.8}$ . It is evident from the figure that the melting point is about 809  $^{\circ}\text{C}$ , which is surprising, because the MP of  $\text{GaTe}$  is about 826  $^{\circ}\text{C}$  and the MP of  $\text{GaSe}$  is about 960  $^{\circ}\text{C}$ .

In conclusion, the feasibility of growing high purity GX crystals ( $\text{X}=\text{Te}$  and  $\text{Se}$ ) and their alloys was successfully demonstrated in the project and preliminary characterization indicates that stoichiometric compounds and large single crystalline sections can be obtained.